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Solubilities of 1-Eicosanol and Eicosanoic Acid in Supercritical Carbon Dioxide from 308.2 to 328.2 K at Pressures to 21.26 MPa

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The solubilities of 1-eicosanol and eicosanoic acid in carbon dioxide have been measured by using a semiflow phase equilibrium apparatus over the temperature range from 308.2 to 328.2 K at pressures up to 212.6 bar. The measured mole fractions of 1-eicosanol and eicosanoic acid are correlated with the reduced density and reduced pressure of carbon dioxide.

Introduction

The phase behavior of low-volatile components in supercritical fluid has received wide attention in recent years for potential applications in industrial fields (*1, 2*). However, limited studies on the solubilities of heavy alcohols and their related fatty acids in carbon dioxide are presented in the literature. Kramer and Thodos (*3, 4*) have measured the solubilities of 1-hexadecanol, 1-octadecanol, palmitic acid, and stearic acid in supercritical carbon dioxide. Schneider et al. (*5–7*) have reported the solubilities of 1-hexadecanol and 1-octadecanol in supercritical carbon dioxide at 333 and 393 K. Giddings et al. (*8, 9*) have measured the solubilities of 1-octadecanol in dense supercritical carbon dioxide at 313 K. Iwai et al. (*10*) have measured the solubilities of 1-octadecanol, 1-eicosanol, and stearic acid in supercritical carbon dioxide at 308.2 K up to 23.7 MPa. Hamatani (*11*) has measured the solubilities of 1-octacosanol and 1-triacontanol in supercritical carbon dioxide. The solubilities of 1-hexadecanol and 1-octadecanol in supercritical carbon dioxide over the temperature range from 302 to 338 K at pressures from 5.0 to 20.5 MPa and the solubilities of lauric acid, palmitic acid, and arachidic acid in carbon dioxide over the temperature range from 373.2 to 473.2 K at pressures up to 5.07 MPa have been measured previously (*12, 13*).

Although some solubility data of heavy alcohols and their related fatty acids in carbon dioxide have been reported, none have been studied in detail from low pressure to high pressure. In this work the solubilities of 1-eicosanol and eicosanoic acid in carbon dioxide over the temperature range from 308.2 to 328.2 K at pressures from 33.7 to 212.6 bar have been measured, and the measured data are correlated by the proposed equations.

Experimental Section

A semiflow phase equilibrium apparatus was used for the measurement of solubilities for 1-eicosanol and eicosanoic acid in carbon dioxide from the subcritical to the supercritical state. The experimental equipment and sampling procedure have been described elsewhere (*12*). Briefly, approximately 27 g of the solute was introduced into the equilibrium cell in solid form at three evenly spaced points separated by 0.2-cm-diameter stainless steel balls. The equilibrium cell consisted of a stainless steel pipe (30 cm in length with a 1.93-cm inner diameter) with reducer–adapter couplings at each end. The cell was inserted into a constant–temperature stirred water bath. The temperature of the water bath was measured with a mercury-in-glass thermometer with 0.1 K accuracy. Liquid carbon dioxide was continuously compressed into the cell by a positive-displacement liquid pump from a cylinder. The pressure of the equilibrium cell was measured by a Heise gauge to ±0.3 bar. All experiments were performed using a carbon dioxide flow rate between 0.2 and 0.6 normal L/min. In this range, tests performed at the same temperature and pressure demonstrated that measured solubilities were not affected by the contacting time between carbon dioxide and the solute. To prevent hydrated formation (*14*), traces of water were removed from the carbon dioxide by a gas purifier placed upstream of the pump. After the flow had passed the equilibrium cell for about 1 h, the saturated carbon dioxide was withdrawn, reduced in pressure, and raised in temperature about 150–200 K above the bath temperature to avoid precipitation of the solute in the line (*15*), and then the solute was collected in a cold trap that was packed with cotton in order to catch the small particles of the solute and was submerged in an ice bath. The liberated carbon dioxide from the trap was measured volumetrically in a wet test meter with an accuracy of 0.1%, and about 0.1 g of the collected solute was weighed by an analytical balance with an accuracy of 0.1 mg.

Materials

The carbon dioxide had a stated minimum purity of 99.5 mol %. The 1-eicosanol was purchased from Sigma and eicosanoic acid from Fluka with a minimum purity of 99 mol %. The chemicals were used without further purification.

Results

Tables 1 and 2 present the solubilities of 1-eicosanol and eicosanoic acid in carbon dioxide, respectively, over the temperature range from 308.2 to 328.2 K at pressures from 33.7 to 212.6 bar. These data are also shown graphically in Figures 1 and 2. Each reported datum is the average value of at least two replicate samples. The sample compositions of the solutes were generally reproducible within ±2% in the mole fraction solubilities of the solutes in carbon dioxide. The solubilities of the solutes increase with pressure in the supercritical state, but the solubilities

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Table 1. Solubility Data y_2 of 1-Eicosanol in Carbon Dioxide and Reduced Densities of Carbon Dioxide $\varrho_{r,1}$ as a Function of Temperature *T* and Pressure *P*

T/K	*P*/bar	10^5y_2	$\varrho_{r,1}$
308.2	37.5	2.23	0.175
	64.6	2.13	0.378
	92.4	7.74	1.481
	116.3	12.38	1.641
	412.3	15.08	1.736
	164.4	18.09	1.786
	186.6	19.40	1.834
	209.0	22.96	1.867
318.2	36.2	2.04	0.154
	63.4	1.49	0.328
	93.7	4.20	0.823
	116.7	20.31	1.341
	140.2	42.44	1.528
	164.4	53.77	1.625
	189.2	60.84	1.701
	212.6	69.86	1.750
328.2	37.5	1.75	0.148
	73.0	1.52	0.351
	89.9	1.60	0.530
	113.7	10.04	0.998
	140.6	67.73	1.320
	161.6	125.77	1.457
	186.8	178.23	1.579
	210.4	221.00	1.650

Table 2. Solubility Data y_2 of Eicosanoic Acid in Carbon Dioxide and Reduced Densities of Carbon Dioxide $\varrho_{r,1}$ as a Function of Temperature *T* and Pressure *P*

T/K	*P*/bar	10^5y_2	$\varrho_{r,1}$
308.2	38.2	1.23	0.179
	70.3	1.27	0.411
	117.1	2.32	1.649
	138.5	3.59	1.724
	163.0	4.69	1.783
	187.1	5.68	1.835
	209.5	6.23	1.868
318.2	37.5	1.12	0.161
	91.9	1.12	0.764
	115.9	2.22	1.332
	139.9	4.52	1.527
	163.3	6.11	1.621
	187.1	8.02	1.698
	210.4	8.90	1.745
328.2	33.7	0.63	0.131
	67.3	0.90	0.315
	91.3	1.68	0.556
	135.9	5.84	1.283
	161.3	10.34	1.455
	188.8	17.87	1.585
	211.2	28.73	1.652

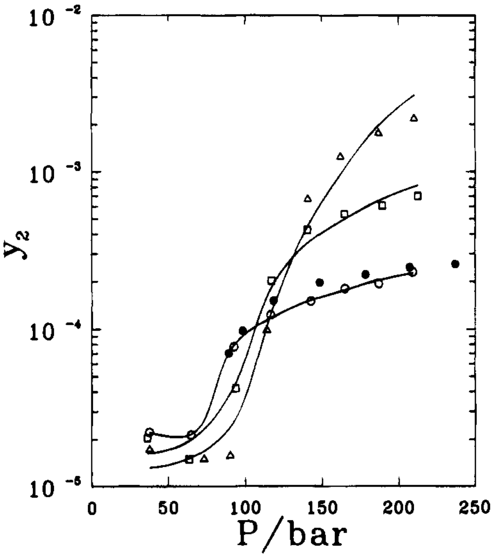

Figure 1. Comparison of the calculated mole fraction y_2 of 1-eicosanol in carbon dioxide with experimental data at different temperatures: (○) 308.2 K, (□) 318.2 K, (△) 328.2 K, (●) 308.2 K (Iwai et al. (*10*)), (—) calculated with eq 2.

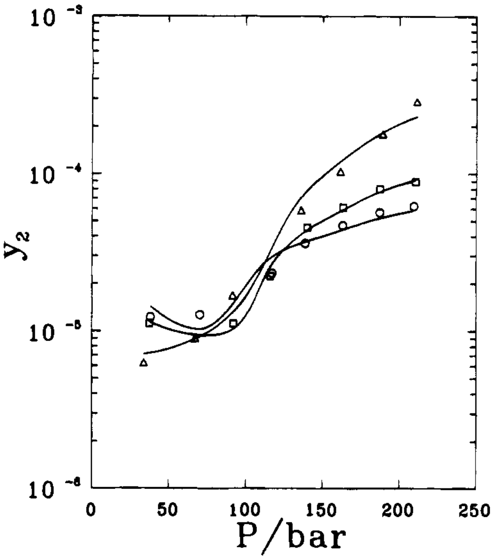

Figure 2. Comparison of the calculated mole fraction y_2 of eicosanoic acid in carbon dioxide with experimental data at different temperatures: (○) 308.2 K, (□) 318.2 K, (△) 328.2 K, (—) calculated with eq 2.

generally decrease with increasing pressure as the pressures are below the critical pressure. From the effect of temperature on the solubilities, we find that the retrograde solubility (crossover pressure) behavior (*16–18*) exists in the supercritical state. Comparing our data with those reported by Iwai et al. (*10*) for carbon dioxide + 1-eicosanol at 308.2 K, we find that the solubilities of this work are lower than those of the literature. The maximum deviation at 150 bar is about 15%.

The reliability of the apparatus was preliminarily tested by measuring the solubilities of naphthalene in supercritical carbon dioxide at 328.2 K. The solubilities obtained were in good agreement with those of Tsekhanskaya et al. (*19*) and Kurnik et al. (*20*). Although the sublimation pressure of 1-eicosanol is lower than that of naphthalene, the temperature of the line after the metering valve was raised about 150–200 K above the bath temperature in order to avoid precipitation of the solute in the line, as suggested by Dimitrelis and Prausnitz (*15*). The reproducibility of the solubilities measured by Iwai et al. (*10*) was ±4% and ±10% when the pressure was higher than 9.0 MPa and lower than 9.0 MPa, respectively. Therefore, we think the experimental data of this work are reasonable.

Correlation

The solubilities of 1-eicosanol and eicosanoic acid in carbon dioxide are correlated by three methods. In the first method the mole fraction of solute, y_2, was related to the reduced density of carbon dioxide, $\varrho_{r,1} = (\varrho_1/\varrho_{c,1})$, with the following equation (*3, 4, 8*):

$$\log y_2 = A + B\varrho_{r,1} \tag{1}$$

The reduced densities of carbon dioxide used in the present study were obtained from the work of Kennedy and Thodos (*21*). These reduced densities are listed in Tables 1 and 2. The calculated results with optimum values of *A* and *B* for each isotherm and for all temperature ranges are listed in Table 3. It can be seen that the average absolute deviations in y_2 are 24.89% (24 points) and 23.17%

Table 3. Correlation of Solubility Data with Three Equations

				eq 1			eq 2				eq 3			
solute	T/K	P range/bar	no. of pts	A	B	$10^2\Delta y_2/y_2$	A	B	C	$10^2\Delta y_2/y_2$	A	B	D	$10^2\Delta y_2/y_2$
1-eicosanol	308.2	37.5−209.0	8	−4.8416	0.5942	15.17	−4.6126	−0.3164	0.4468	2.38	−4.7394	0.7497	1.976	5.87
	318.2	36.2−212.6	8	−5.0709	1.0776	21.72	−4.8368	0.2433	0.4317	14.96	−4.9615	1.1915	1.439	18.43
	328.2	37.5−210.4	8	−5.3406	1.6035	37.79	−4.9172	0.1314	0.8035	24.96	−5.0742	2.0343	2.266	32.50
	overall	36.2−212.6	24			24.89				13.88				18.93
eicosanoic acid	308.2	38.2−209.5	7	−5.0267	0.3727	21.51	−4.6847	−1.0115	0.6708	12.21	−4.9262	0.8963	9.90	5.74
	318.2	37.5−210.4	7	−5.2206	0.5972	31.57	−4.8474	−0.6856	0.6584	5.53	−4.9855	1.5308	15.70	13.10
	328.2	33.7−211.2	7	−5.3606	1.0025	16.43	−5.2015	0.3751	0.3461	13.62	−5.1339	1.6449	4.80	8.00
	overall	33.7−211.2	21			23.17				10.45				8.95

(21 points) for carbon dioxide + 1-eicosanol and carbon dioxide + eicosanoic acid, respectively. The calculated deviations were too large, so alternative methods were considered.

The second method is similar to the first, with the addition of a $\varrho_{r,1}{}^2$ term:

$$\log y_2 = A + B\varrho_{r,1} + C\varrho_{r,1}{}^2 \qquad (2)$$

The optimum values of A, B, and C for each isotherm are listed in Table 3. The average absolute deviations of 13.88% (24 points) for carbon dioxide + 1-eicosanol and 10.45% (21 points) for carbon dioxide + eicosanoic acid indicate a considerable improvement over eq 1. These calculated results are shown in Figures 1 and 2.

Because the solubilities decrease with increasing pressure in the subcritical state, the total pressure of the system may be introduced in the third method. We express the method as follows:

$$\log y_2 = A + B\varrho_{r,1}/D^{1/P_{r,1}} \qquad (3)$$

where $P_{r,1}$ is the reduced pressure of carbon dioxide.

The optimum values of A, B, and D for each isotherm and for all temperature ranges are also given in Table 3. The average absolute deviation for carbon dioxide + 1-eicosanol was found to be 18.93% (24 points), while that for carbon dioxide + eicosanoic acid was 8.95% (21 points). Table 3 indicates that the calculated results by using eqs 2 and 3 for carbon dioxide + 1-eicosanol and carbon dioxide + eicosanoic acid give satisfactory agreement with experimental data.

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